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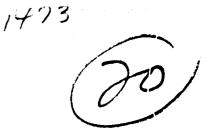
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(TITLE UNCLASSIFIED)

INVESTIGATION OF THE THERMODYNAMIC PROPERTIES OF PROPELLANT INGREDIENTS

FINAL FEBRUARE REPORT, AFR

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(Prepared under Contract Nr FØ4611-67-C-Ø925)

The Dow Chemical Company,

Midland, Michigan 48640)

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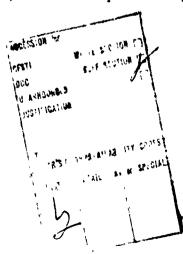
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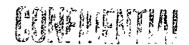
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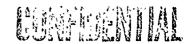
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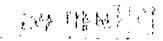
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#### FOREWORD



This report was prepared by The Dow Chemical Company, Midland, Michigan, under USAF Contract F04611-67-C-0025. The contract was initiated under Air Force Program 750 G, AFSC Project 3148, "Investigation of the Thermodynamic Properties of Propellant Ingredients and the Burning Mechanisms of Propellants." The work was administered under the direction of the Rocket Propulsion Laboratory, Edwards Air Force Base, with Mr. Curtis C. Selph acting as Air Force Project Officer.

This final report covers the work performed during <u>l January</u> 1967 through 30 June 1969. The Dow Report Number is T0025-F-69.

This work was performed by Dr. G. C. Sinke and Dr. J. L. Curnutt, under the technical supervision of Dr. D. R. Stull and Dr. H. Prophet and management supervision of Dr. K. O. Groves.

This report has been reviewed and is approved.

W. H. Ebelke, Colonel, USAF Chief, Propellant Division

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#### ABSTRACT

- (C) The heats of formation of methylene bisoxyamine  $(CH_6N_2O_2)$ and methylene bisoxyamine diperchlorate (CH<sub>6</sub>N<sub>2</sub>O<sub>2</sub>·2HClO<sub>4</sub>) were derived from oxygen bomb combustion calorimetry and solution calorimetry. Selected best values for the two compounds are -22.4 kcal/mole for liquid methylene bisoxyamine and -103.0 kcal/mole for crystalline methylene bisoxyamine diperchlorate.
- (C) A technique for obtaining heats of formation of gaseous C-H-O-N-F compounds was developed, with CF3CN as a reference substance. When the technique was applied to  $F_2C(ONF_2)_2$ , results deviated widely from the expected range. Chromatographic examination revealed a large fraction of F3CONF2 was present in the sample and no accurate result for  $F_2C(ONF_2)_2$  could be derived. The amount of sample available was too small to allow purification.

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#### (U) THERMOCHEMISTRY

# A. THE HEATS OF FORMATION OF METHYLENE BISOXYAMINE AND METHYLENE BISOXYAMINE DIPERCHLORATE (C)

#### 1. Introduction (U)

(C) Samples of methylene bisoxyamine (hereafter referred to by code letters DO) and methylene bisoxyamine diperchlorate (code letters DOAP) were received from Dr. Claude Merrill of the Air Force Rocket Propulsion Laboratory, Edwards Air Force Base, California. The samples were investigated by both oxygen bomb and solution calorimetry.

#### 2. Materials (U)

- (U) DO is a colorless liquid, reported by AFRPL to be flammable and to have an impact sensitivity of 70 kg-cm and a vapor pressure of 1 mm at 33°C. It is somewhat hygroscopic and was transferred only in a dry nitrogen atmosphere. It is decomposed catalytically by a number of substances. The present sample was stated on the basis of vapor phase chromatography to be of higher purity than the 99.1% material for which data were reported earlier (1).
- (U) DOAP was a white crystalline solid. According to Dr. Merrill, elemental analyses for carbon, hydrogen, and nitrogen were in good accord with theory. The compound was transferred only in a dry nitrogen atmosphere. An analysis for perchlorate ion at Dow gave 71.15%  $C10\frac{7}{4}$  versus theory of 71.29%.
- (U) Ethylene glycol was used as a solvent for both DO and DOAP. The glycol is hygroscopic and between the two investigations it picked up enough water to change its heat of combustion appreciably. The heat of combustion of the glycol was therefore measured twice, once at the time of DO experiments and once at the time of the DOAP experiments.

#### Equipment (U)

(U) A rotating bomb calorimeter and a platinum-lined bomb were employed for heat of combustion work. A simple glass Dewar calorimeter was used for heats of solution. A Beckman microcalorimeter was used for the heat of mixing of DO and ethylene glycol.

#### 4. Procedure (U)

(U) Preliminary experiments showed both DO and DOAP detonated to incomplete combustion products when ignited in a platinum crucible in a bomb charged with oxygen at 30 atm pressure. Suitable moderation of the combustion reaction was achieved by burning a 50-50 mixture of DO or DOAP with ethylene glycol.

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- (U) A long narrow bag open on both ends was fabricated from 0.5 mil polypropylene film and accurately weighed. A clamp was fastened across the middle of the bag and the assembly weighed. An appropriate amount of DO or DOAP was added to one side of the bag; this transfer was carried out in a dry nitrogen atmosphere. The end of the bag was heat sealed, and the bag assembly was removed from the dry box and weighed to determine the amount of DO or DOAP added. Ethylene glycol was then added to the other side of the bag, which was heat sealed and weighed to determine the exact amount of glycol added. After visual inspection and absence of weight loss had established that the bag was not leaking, the clamp was removed and the contents of the bag mixed by gentle manipulation.
- (U) The bag was next folded into a platinum crucible which was suspended in a gimbal in the combustion bomb. A cotton thread fuse was strung from a fine platinum ignition wire to the bag. For DO experiments, 1.0 ml of water was added to the bomb; for DOAP runs, approximately 1l g of 0.08 M As<sub>2</sub>O<sub>3</sub> solution was added from a weight buret. The bomb was closed and charged with purified oxygen to 30 atm pressure. After thermal equilibrium was established, the charge was fired by electrical heating of the fuse wire, and the resulting temperature rise was accurately monitored by an automatic resistance bridge. After the calorimetry the bomb was slowly discharged, opened, and washed out with hot distilled water. The washings were analyzed for nitrate and, in the case of DOAP, also for As<sub>2</sub>O<sub>3</sub> and dissolved platinum.
- (U) The heat of combustion of ethylene glycol was measured in the same apparatus. The conditions for the glycol experiments (such as loading and weighing times) were kept as nearly as possible identical to the DO-glycol experiments to eliminate systematic errors. The heats of combustion of the polypropylene film and cotton fuse were reported earlier (1).
- (U) Heats of mixing of DO and DOAP in 1 N perchloric acid were measured in a simple Dewar vessel calorimeter equipped with a heater, stirrer, and thermometer. Samples of 1 to 2 g were sealed in thin walled glass ampoules which were immersed in 1 liter of aqueous acid. After thermal equilibrium had been established, the ampoule was broken by means of a push rod and the resulting temperature change recorded. The calorimeter was calibrated by addition of electrical energy. The heat of mixing of DOAP and ethylene glycol was derived from measurements of the heats of solution of DOAP, ethylene glycol, and of the 50-50 DOAP-glycol mixture in aqueous 1 N perchloric acid.
- (U) The heat of mixing of DO and ethylene glycol was observed directly in a Beckman microcalorimeter (1).

#### 5. Calculations (U)

- (U) A number of corrections must be applied to the bomb calorimeter data in order to derive true heats of formation. These corrections are calculated by means of a computer program based on the outline of Hubbard et al. (2) for C-H-O and C-H-O-N compounds and of Baroody et al. (3) for C-H-O-N-Cl compounds. Parameters for C-H-O-N compounds are reasonably well established, but for C-H-O-N-Cl some estimates have to be made (4). Constant factors specific for the individual compounds DO, DOAP, and glycol are given in Table I.
- The calorimeter equivalents, E (calor), were determined by combustion of benzoic acid and are averages of numerous determinations.

#### 6. Results (U)

- (C) Calorimetric data for methylene bisoxyamine are given in Table II. The correction for ethylene glycol is taken from data in Table III.
- (C) To the average result of Table II is added the heat of mixing of 5.3 cal/g to give  $-\Delta E \& /M = 3539.0$  cal/g. The molecular weight of methylene bisoxyamine is 78.071 which yields:

$$\Delta E \& 298 = 276.29 \pm 0.37 \text{ kcal/mole}$$

for the reaction:

$$CH_6N_2O_2(l) + 3/2 O_2(g) \rightarrow CO_2(g) + 3H_2O(l) + N_2(g)$$

Calculating to constant pressure conditions:

$$\Delta H_{298} = -276.59 \pm 0.37 \text{ kcal/mole}$$

from which is derived:

$$\Delta \text{Hf}_{298}^{\circ}(\ell) = -22.4 \pm 0.37 \text{ kcal/mole}$$

The uncertainty is twice the standard deviation.

(C) Calorimetric data for methylene bisoxyamine diperchlorate are given in Table IV. Correction for ethylene glycol is based on data in Table V. The average result of Table IV and a molecular weight of 278.988 yield:

$$\Delta E8 = -276.86 \pm 1.48 \text{ kcal/mole}$$

for the reaction:

$$CH_8Cl_2N_2O_{10}(in glycol) \rightarrow CO_2(g) + 2HCl(600H_2O) + 3H_2O(l) + N_2(g) + 5/2 O_2(g)$$

## Table I

(c)	Constant Factors in Combustion	Calorimetry of DO and DOAPa
	Empirical formula, DO	$CH_6N_2O_2$
	Empirical formula, DOAP	$\mathrm{CH_8Cl_2N_2O_{10}}$
	Empirical formula, glycol	C <sub>2</sub> H <sub>6</sub> O <sub>2</sub>
	Density of DO, g/cc	1.100
	Density of DOAP, g/cc	(1.85)
	Density of glycol, g/cc	1.115
	Bomb volume, liter	0.349
	Water added to bomb for DO and glycol, ml	1.0
	Initial oxygen pressure at 25°C, atm	30.3
	Reference temperature, °C	25.00
	Final ratio H2O/HCl for DOAP	600
	$\left(\frac{\partial E}{\partial P}\right)_{\mathrm{T}}$ of DO, cal/g/atm	(-0.003)
	$\left(\frac{\partial E}{\partial P}\right)_{\mathrm{T}}$ of DOAP, cal/g/atm	(-0.001)
	$\left(\frac{\partial E}{\partial P}\right)_{\mathrm{T}}$ of glycol, cal/g/atm	-0.00397
	C <sub>p</sub> of DO, cal/g/°C	(0.50)
	C <sub>p</sub> of DOAP, cal/g/°C	(0.26)
	C <sub>p</sub> of glycol, cal/g/°C	0.577
	E(calor), cal/°C	3427.20
	Added platinum parts, g	47.33

 $<sup>^{\</sup>rm a}$ Quantities in parentheses are estimated.

Table II

(C) Combustion Experiments on Methylene Bisoxyamine (DO)

		Ξ	Experiment Number		
Parameter	1	<i>ا</i> له	3	17	5
DO mass, g	0.49928	0.51027	0.52140	0.52723	0.52010
Glycol mass, g	0.83184	0.87451	0.84:927	0.85420	0.73021
Film mass, g	0.10389	0.09705	0.10592	0.10240	0.12076
Fuse mass, g	0.00386	0.00301	0.00365	0.00379	0.00385
ti, °C	22.96676	22.96674	22.96672	22.96670	22.96674
tf, °C	24.98489	25.02581	25.03119	25.03107	24.93344
Δt Orn °C	0.06858	0.06530	0.06176	0.06159	0.07397
$\mathcal{E}_{i}$ (cont), cal/°C	5.658	5.684	5.680	5.684	5.649
$\mathcal{E}_{ m f}$ (cont.), cal/°C	6.179	6.215	5.924	5.934	5.865
Corr. to std. states, cal	3.114	3.226	3.220	3.202	2.954
Ignition energy, cal	0.36	92.0	0.32	0.37	0.41
ΔEHNO. cal	12.456	12.244	12.244	14.215	12.104
-∆E°/M, cal/g	3533.8	5554.1	3542.2	3530.4	3528.1

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verage  $-\Delta E_c^{\circ}/M$  = 5535.7 cal/g,  $\sigma$  = 2.4 cal/g

 $^{\rm a}{\rm Includes}$  Items 81-85 and 87-94 of Reference 2.

Table III

U) Heat of Combustion of Ethylene Glycol for DO Experiments

	Expe	Experiment Number	•
Parameter	6	10	1.1
Sample mass, g	1.38125	1.39260	1.36154
Polypropylent, g	0.07482	0.07219	0.09922
Cotton fuse, g	0.00362	0.00318	0.00236
t <sub>i</sub> , °C	22.96679	22.96664	22.96676
tf, °C	25.08628	25.09333	25.13661
$\Delta t_{ ext{corr}}$ , °C	0.06020	0.06252	0.05671
Ign. Energy, cal	0.36	0.36	0.38
Corr. to std. states, cala	3.561	3.581	3.612
$\xi_{ m i}$ (cont.), cal/°C	5.701	5.707	5.727
$\mathcal{E}_{ m f}$ (cont.), cal/°C	6.231	6.237	6.274
$-\Delta E_{g}/M$ , cal/g	4504.9	4502.4	4503.5

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m a}_{
m Includes}$  Items 81-85 and 87-94 of Reference 2.

(C) Heat of Combustion of Methylene Bisoxyamine Diperchlorate

		ΕX	Experiment Number		
Parameter	7	N	3	4	5
Sample mass, g	0.50090	0.49822	0.51089	0.49928	0.50170
Glycol mass, g	1.21573	1.09178	1.13825	1.14813	1.14898
Polypropylene mass, g	0.09441	0.09461	0.07988	0.08772	0.09170
Cotton fuse mass, g	0.00442	0.00387	0.00344	0.00408	0,00340
$n^{i}$ (H <sub>2</sub> O), mole	0.6522	0.5952	0.6410	0.6116	0.6169
ni (As <sub>203</sub> ), mole	0.001243	0.001135	0.001227	0,001170	0.001174
$ m n^f$ (As <sub>2</sub> O <sub>3</sub> ), mole	0.001162	0.001019	0.001144	0.001106	0.001125
$n_{1}^{\mathrm{f}}$ (HNO <sub>3</sub> ), mole	0.000516	0.000520	0.000508	0.000504	0.000540
$n^{1}$ (H <sub>2</sub> PtCl <sub>6</sub> ), mole	0.000011	0.000011	0.000010	0.00000	0.000007
ti, °c	22.96678	22.96678	22.96677	22.96033	22.96677
o, t <sub>t</sub> ,	25.08450	24.93516	24.94820	24.97982	24.99362
$^{\Delta t}_{corr.}$ , $^{\circ}c$	0.06302	0.07472	0.07138	0.07469	0.06758
Ign. energy, cal	0.39	0.36	0.37	0.39	0.39
Corr. to std. state, cal	7.736	974.9	7.142	7.076	7.147
${\cal E}_{ exttt{i}}( ext{cont.})$ , $ ext{cal}/ ext{°C}$	16.422	15.332	16.173	15.656	15.753
$\mathcal{E}_{ m f(cont.)}$ , cal/°C	16.821	15.685	16.534	16.031	16.136
$-\Delta E_c/M$ , cal/g	499.2	492.5	4.703	493.6	499.2

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<sup>a</sup>Includes Items 81-85, 87-89, 93, and 94 of Reference 2.

Table \

(U) Heat of Combustion of Ethylene Glycol for DOAP Experiments

			H	Experiment Number		
	Parameter	1	a	2	4	5
	Sample mass, g	1.36266	1.36609	1.35999	1.36760	1.35481
	Polypropylene, g	0.05588	0.06923	0.05754	0.06102	0.06519
	Cotton fuse, g	00,000,00	0.00378	0.00392	0.00346	0.00400
C	ti, °C	22.96673	55.96669	22.96672	22.96684	23.00462
)		25.01884	25.06089	25.01880	25.03658	25.06574
N		0.06934	0.06544	0.06950	0.06488	0.05931
FI		0.35	0.36	0.36	0.28	0.32
-8- <b>D</b>		3.425	5.493	3.425	3.460	3.444
EI	${\cal E}_{ m i}$ (cont.), cal/°C	5.681	5.687	5.680	5.685	5.679
V1		6.186	6.206	6.186	6.197	6.191
ΓI	$-\Delta E_{c}^{\circ}/M$ , cal/g	4526.4	4523.0	4521.6	4525.5	4524.9
ΑL		Average $-\Delta E_{\rm c}^{\circ}/$	Average $-\Delta E_c^{\circ}/M = 4524.3 \text{ cal/g}$			

 $^{
m a}_{
m Includes}$  Includes Items 81-85 and 87-94 of Reference 2

Correcting to constant pressure conditions:

$$\Delta \text{He}_{298}^{\circ} = -276.86 + 9/2 \text{ RT}$$
  
= -274.20 \pm 1.48 kcal/mole

(C) Before proceeding to heat of formation calculations, the heat of solution results will be presented. Duplicate determinations agreed to within ±0.2 kcal/mole for the following heats of solution in 1 N HClO4:

ΔH sol'n, kcal/mole
-13.6
+ 5.1
- 1.35
+ 6.5

The difference in the heat of solution of crystalline DOAP and DOAP dissolved in glycol gives the heat of solution of DOAP in glycol as -1.4 kcal/mole. The heat of combustion of crystalline DOAP is therefore:

$$\Delta H_{c_{298}}$$
 (c) = -274.20 - 1.40 kcal/mole  
= -275.60 ± 1.48 kcal/mole

The heat of formation of methylene bisoxyamine perchlorate is calculated from this value and heats of formation of  ${\rm CO_2}$ , HCl (in  ${\rm 600H_2O}$ ) and H<sub>2</sub>O as:

$$\Delta \text{Hf}^{\circ}_{298}(c) = -103.0 \pm 1.5 \text{ kcal/mole}$$

(C) The above heats of solution provide a cross-check on the heat of combustion results. From National Bureau of Standards Technical Note 270-3 the heat of formation of 1 N  $HC10_4$  is -30.96 kcal/mole. The following reaction scheme can be written:

$$CH_6N_2O_2(l) + 2HClO_4(aq) \rightarrow [CH_6N_2O_2 \cdot 2HClO_4] (aq)$$
 
$$\Delta H = -13.6 \text{ kcal}$$
 
$$CH_6N_2O_2 \cdot 2HClO_4(c) \rightarrow [CH_6N_2O_2 \cdot 2HClO_4] (aq)$$
 
$$\Delta H = +5.1 \text{ kcal}$$

adding algebraically:

$$CH_6N_2O_2(l) + 2HClO_4(aq) \rightarrow CH_6N_2O_4 \cdot 2HClO_4(c)$$
  
 $\Delta H = -18.7 \text{ kcal}$ 

Therefore the difference between the heats of formation of methylene bisoxyamine and its diperchlorate should be:

 $\Delta H = -18.7 + 2(-30.96)$ = -80.6 kcal

The difference from combustion calorimetry is:

 $\Delta H = -103.0 - (-22.4)$ = -80.6 kcal

The exact agreement is of course fortuitous, but does demonstrate the consistency of the thermochemical network and indicates the individual values are highly reliable.

#### B. ATTEMPTED MEASUREMENT OF THE HEAT OF FORMATION OF F2C(ONF2)2 (C)

#### 1. Introduction (U)

(C) A one gram sample of  $F_2C(ONF_2)_2$  was received from Dr. Pilipovich of Rocketdyne Corporation. According to Dr. Pilipovich, the infrared spectrum of the sample was identical to that cf highly pure material he had prepared previously. Because of the limited amount of sample and limited time available, no attempt was made to further establish the purity and the sample was used as received.

#### 2. Method (U)

- (C) A technique for carrying out an explosion reaction in a combustion bomb, followed by the addition of water to the bomb from an annular tank, was developed some years ago. A description of the technique as applied to the reaction of NF3 and H2 has been published (5). For  $F_2C(ONF_2)_2$ , it was believed that a mixture with H2 and O2 would give an explosive mixture yielding HF,  $CO_2$  and  $N_2$  with perhaps some  $HNO_3$ . However, it was found that H2 and O2 react slowly to form water in a platinum lined bomb. A sample of high purity propane was substituted for hydrogen; this had the advantage that the propane could be condensed in a steel cylinder and weighed.
- (U) To check out this technique, a sample of high purity  $CF_3CN$  was exploded with about an equal amount of propane and a twofold excess of oxygen. Infrared examination of the bomb gases showed only  $CO_2$ ; no trace of  $CF_4$  was observed. The heat of the explosion was measured and a heat of formation calculated for  $CF_3CN$  in good agreement with a value obtained from the heat of reaction of  $CF_3CN$  and  $NF_3$  (6). The technique was therefore regarded as satisfactory.

#### 3. Results (U)

(C) Two explosions on samples of about 0.3g were carried out. The heats of reaction were far less than expected for  $F_2C(ONF_2)_2$ ; in addition, the molecular weight of the material

calculated from the pressure, the bomb volume, and the ambient temperature was far below theory. The remaining sample was therefore examined by vapor phase chromatography which showed about 10% of  $F_3CONF_2$  to be present. Ordinarily, one might be able to correct for this impurity; however, it appears that the original sample was partially condensed in the steel cylinder and the gas phase was much richer in  $F_3CONF_2$  than the liquid. Thus, the first explosion experiment probably involved 50% or more of  $F_3CONF_2$ , the second about 20%, and the remaining sample still had 10%  $F_3CONF_2$ . No accurate single composition could therefore be derived. It seems clearly impossible to derive any satisfactory heat of formation from the data obtained.

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# UNCLASSIFIED AFRPL-TR-69-183

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